

# Discontinuous liquid rise in capillaries with nonuniform cross-sections

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We consider theoretically liquid rise against gravity in capillaries with height-dependent cross-section. For a conical capillary made from a hydrophobic surface and dipped in a liquid reservoir, the equilibrium liquid height depends on the cone opening angle  $\alpha$ , the Young-Dupré contact angle  $\theta$ , the cone radius at the reservoir's level  $R_0$  and the capillary length  $\kappa^{-1}$ . As  $\alpha$  is increased from zero, the meniscus' position changes continuously until, when  $\alpha$  attains a critical value, the meniscus jumps to the bottom of the capillary. For hydrophilic surfaces the meniscus jumps to the top. The same liquid height discontinuity can be achieved with electrowetting with no mechanical motion. Essentially the same behavior is found for two tilted surfaces. We further consider capillaries with periodic radius modulations, and find that there are few competing minima for the meniscus location. A transition from one to another can be performed by the use of electrowetting. The phenomenon discussed here may find uses in microfluidic applications requiring the transport small amounts of water "quanta" (volume < 1 nL) in a regular fashion.

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The behavior of liquids confined by solid surfaces is important in areas such as microfluidics [1, 2], wetting of porous media [3], the creation of hydrophobic surfaces [4, 5], oil recovery [6] and water transport in plants [7]. As the system size is reduced, the interfacial tensions become increasingly important in comparison to bulk energies, and are essential in understanding the equilibrium states as well as the system dynamics.

Wetting has been studied for liquids in contact with curved surfaces [1, 8, 9, 10], wedges [11, 12] and cones [13, 14, 15], and topographically [16] or chemically modulated substrates [17, 18, 19, 20]. However, surprises appear even for very simple geometries of the bounding surfaces. Here we focus on the rise of a liquid in capillaries with nonuniform cross-sections. When a solid capillary is immersed in a bath of liquid, the height of the contact line above the bath level  $h$  is given by

$$h = c\kappa^{-2} \cos \theta / R \quad (1)$$

where  $\kappa^{-1} \equiv (\sigma/g\rho)^{1/2}$  is the capillary length,  $\sigma$  is the liquid-gas interfacial tension,  $\rho$  is the liquid mass density (gas density neglected),  $g$  is the gravitational acceleration, and  $\theta$  is the Young-Dupré contact angle given by  $\cos \theta = (\gamma_{gs} - \gamma_{ls})/\sigma$ , where  $\gamma_{gs}$  and  $\gamma_{ls}$  are the gas-solid and liquid-solid interfacial tensions, respectively [1]. The constant  $c$  is  $c = 2$  for a cylindrical capillary, in which case  $R$  is the radius, or  $c = 1$  for two parallel and flat surfaces separated at distance  $2R$ . The liquid is sucked upwards if the capillary's surface is hydrophilic ( $\theta < \frac{1}{2}\pi$ ), and is depressed downwards in the case of a hydrophobic surface ( $\theta > \frac{1}{2}\pi$ ) [21].

Suppose now that the capillary walls are not vertical, but rather have some opening angle  $\alpha$  as is illustrated in Fig. 1. What is the liquid rise then? One can naively expect that if  $\alpha$  is small,  $h$  changes from Eq. (1) by a

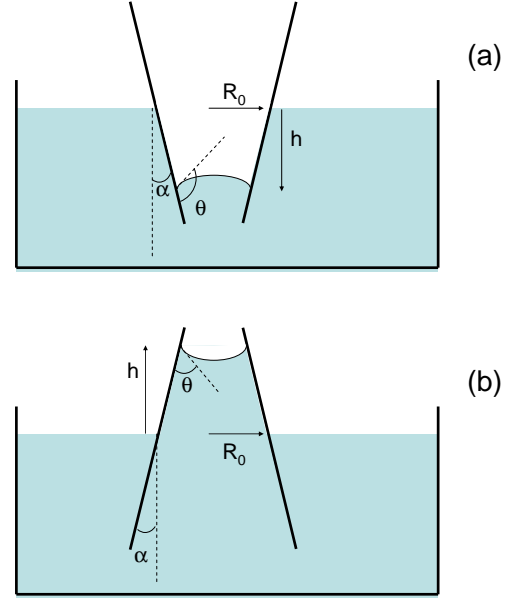


FIG. 1: Schematic illustration of cone capillary or two tilted planes, and definitions of parameters. Two of the possible cases: (a) hydrophobic surface,  $\cos \theta < 0$ , positive opening angle  $\alpha$  and negative  $h$ . (b) hydrophilic surface,  $\cos \theta > 0$ , negative  $\alpha$  and positive  $h$ .

small amount proportional to  $\alpha$ ; it is not even a-priori clear whether  $h$  increases or decreases. We restrict ourselves to narrow capillaries, where  $\kappa R \ll 1$  is satisfied. In this case, as will be verified below, the height is larger than the radius,  $h \gg R$ , and the height variations of the meniscus surface are negligible compared to the total height.

In mechanical equilibrium, at the contact line the

Laplace pressure is balanced by the hydrostatic pressure

$$P_0 + \frac{c\sigma}{r} = P_0 - \rho gh \quad (2)$$

where  $P_0$  is the ambient pressure and  $r$  is the inverse curvature, and is given by  $r(h) = -R(h)/\cos(\theta + \alpha)$ . We denote  $R_0$  as the radius at the bath level (see Fig. 1), and hence  $R(h) = R_0 + h \tan \alpha$ .

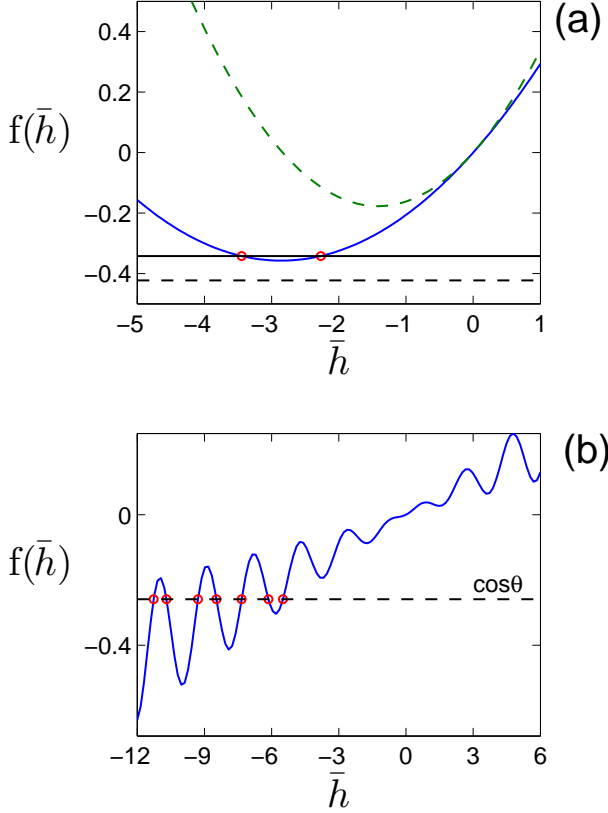


FIG. 2: (a) Solid curved line is a plot of  $f(\bar{h})$  from Eq. (4) and solid horizontal line is  $\cos(\theta + \alpha)$ . Their intersection occurs at two points  $h_1$  (the meniscus location) and  $h_2 < h_1$  marked with circles.  $\bar{R}_0 = 0.5$ ,  $c = 2$  and  $\alpha = 0.087$  ( $5^\circ$ ). Dashed lines are the same, but  $\alpha$  is twice as large,  $\alpha = 0.174$  ( $10^\circ$ ), above the critical angle. In this case there is no solution to Eq. (3), and the meniscus jumps down to the bottom of the capillary. (b) Plot of  $f(\bar{h})$  in the case of periodically-modulated capillary [Eq. (8)]. The horizontal dashed line is  $\cos \theta$ , and the multiple intersections give the possible meniscus locations.  $c = 2$ ,  $\bar{R}_0 = 0.07$ ,  $\bar{R}_m = \bar{R}_0/2$  and  $\mu = 3$ .

We therefore find that the liquid rise is given by

$$\cos(\theta + \alpha) = f(\bar{h}) \quad (3)$$

$$f(\bar{h}) = \frac{1}{c} \bar{h} (\bar{R}_0 + \bar{h} \tan \alpha) \quad (4)$$

where the dimensionless variable  $\bar{h} \equiv \kappa h$  and  $\bar{R}_0 \equiv \kappa R_0$  have been used. These equations reduce to the familiar form Eq. (1) in the limit  $\alpha \rightarrow 0$ . Let us concentrate

first on the case where  $\alpha$  is positive and the surface is hydrophobic,  $\cos \theta < 0$  [see Fig. 1 (a)]; the results for  $\alpha < 0$  follow immediately. The left hand-side of Eq. (3) is then negative for small enough values of  $\alpha$ , and the quadratic form of  $f(\bar{h})$  means that the two solutions  $h_1$  and  $h_2$  are negative, see Fig. 2 (a). The stable solution is  $h_1$  while  $h_2 < h_1$  is unstable.

If the opening angle  $\alpha$  is too large, however, the minimum of  $f(\bar{h})$ , attained at  $\bar{h}^* = -\bar{R}_0/(2 \tan \alpha)$ , is  $f(\bar{h}^*) = -\bar{R}_0^2/(4c \tan \alpha) > \cos(\theta + \alpha)$ , and there is no solution. Hence, for a given value of contact angle  $\theta$ , the critical value of the opening angle  $\alpha_c$  is given by the condition  $f(\bar{h}^*) = \cos(\theta + \alpha_c)$ . As  $\alpha$  is increased past  $\alpha_c$ , the meniscus “jumps” all the way to the bottom of the capillary; in the case of a nearly closed capillary this occurs at  $\bar{h} = 2\bar{h}^*$ .

When the surface is hydrophilic and both  $\theta$  and  $\alpha$  are small, then there is always a positive solution for  $\bar{h}$ . However, if  $\theta < \frac{1}{2}\pi$  but  $\theta + \alpha > \frac{1}{2}\pi$ , the liquid height is negative and the jump again is possible. In essence the capillary behaves as a hydrophobic surface.

A different approach, potentially useful in applications, is that of electrowetting. In the experimental setup the opening angle  $\alpha$  is fixed, but the contact angle may be changed with an external potential  $V$  imposed on the walls:  $\theta = \theta(V)$ . The change to  $\cos \theta$  is  $\varepsilon V^2/(2\sigma \lambda_D) \sim 0.3V^2$  (where  $V$  is in Volt) [24, 25, 26], and thus can be quite large (we took the dielectric constant of water and the Debye screening length  $\lambda_D = 10$  nm). At a fixed value of  $\alpha$ , an increase in  $\theta$  lowers the liquid height until  $\theta$  reaches  $\theta_c$  given by

$$\theta_c = \arccos(-\bar{R}_0^2/(4c \tan \alpha)) - \alpha \quad (5)$$

At all  $\theta > \theta_c$  the meniscus jumps again to the bottom of the capillary. However, if  $\alpha < \alpha^*$ , where  $\alpha^*$  is given by

$$\sin \alpha^* = \bar{R}_0^2/4c, \quad (6)$$

the liquid height is a continuous function of  $\theta$  at all  $\theta$ . The threshold angle  $\alpha^*$  is quite small; if  $\bar{R}_0 = 0.1$  we find  $\alpha^* = 1.25 \cdot 10^{-3}$  ( $0.07^\circ$ ).

Figure 3 (a) is a phase-diagram in the  $\alpha$ - $\theta$  plane. In the region marked “continuous” and for positive  $\alpha$ ,  $\bar{h}(\alpha, \theta)$  changes continuously. Across the critical line  $\theta_c(\alpha)$  [Eq. (5)],  $\bar{h}$  changes discontinuously (meniscus is at the bottom of the capillary). Figure 3 (b) shows the height  $\bar{h}$  as a function of  $\theta$  at fixed value of  $\alpha$ . The meniscus height  $\bar{h}$  decreases below zero until, at the critical value of  $\theta$ , its height jumps from  $\bar{h}^*$  to the capillary bottom (at  $2\bar{h}^*$  if the capillary is nearly closed). Further increase of  $\theta$  does not change the meniscus’ location.

The liquid behavior in capillaries with negative  $\alpha$  [Fig. 1 (b)] follows from the symmetry of the problem: the transformation  $\alpha \rightarrow -\alpha$  and  $\theta \rightarrow \pi - \theta$  leaves Eqs. (3) and (4) unchanged if  $\bar{h} \rightarrow -\bar{h}$ . For negative values of  $\alpha$ , a decrease of  $\theta$  from large values to small ones past  $\theta_c$  leads to a jump of the meniscus to the top of the capillary.

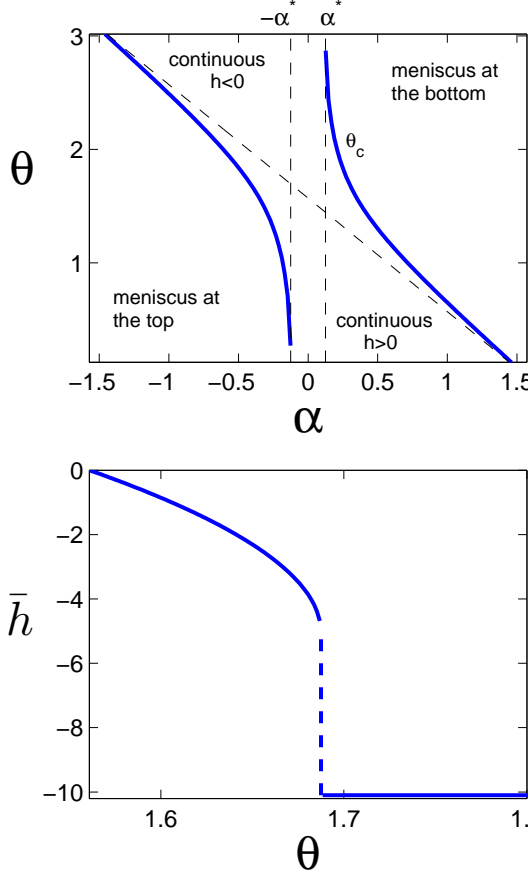


FIG. 3: (a) Phase-diagram in the opening angle-contact angle ( $\alpha$ - $\theta$ ) plane. For positive  $\alpha$ , solid line is  $\theta_c(\alpha)$  from Eq. (5), separating two regions: below it, the meniscus height  $\bar{h}$  changes continuously as a function of  $\alpha$  and  $\theta$ .  $\bar{h}$  is positive if  $\frac{1}{2}\pi - \alpha > \theta$ , negative if  $\frac{1}{2}\pi - \alpha < \theta < \theta_c$ , and zero when  $\theta + \alpha = \frac{1}{2}\pi$  (dashed diagonal line). At a given opening angle  $\alpha$ , increase of  $\theta$  past  $\theta_c$  leads to a jump down of the meniscus from  $\bar{h} = \bar{h}^* < 0$  to the bottom of the capillary. Above the critical line the meniscus is at the bottom. For all angles  $\alpha < \alpha^*$  (see text) the behavior is continuous. The phase-diagram is symmetric with respect to  $\alpha \rightarrow -\alpha$ ,  $\theta \rightarrow \pi - \theta$  and  $\bar{h} \rightarrow -\bar{h}$ . Parameters are  $\bar{R}_0 = 1$  and  $c = 2$ . (b) Meniscus location  $\bar{h}$  as a function of the contact angle  $\theta$  at fixed  $\alpha = 0.01$ ,  $c = 2$  and  $\bar{R}_0 = 0.1$ .

The above insight can be used to exploring different capillaries, and we briefly mention a capillary with periodic width modulations [27, 28], namely  $R(h) = R_0 + R_m \sin(qh)$ , where  $R_m$  is the modulation amplitude and  $q$  its wavenumber. We restrict ourselves to the long wavelength regime, where  $qR_m \ll 1$ . In this case it can be shown that the governing equations replacing Eqs. (3) and (4) are

$$\cos \theta = f(\bar{h}) \quad (7)$$

$$f(\bar{h}) = \frac{1}{c} \bar{h} (\bar{R}_0 + \bar{R}_m \sin(\mu \bar{h})) \quad (8)$$

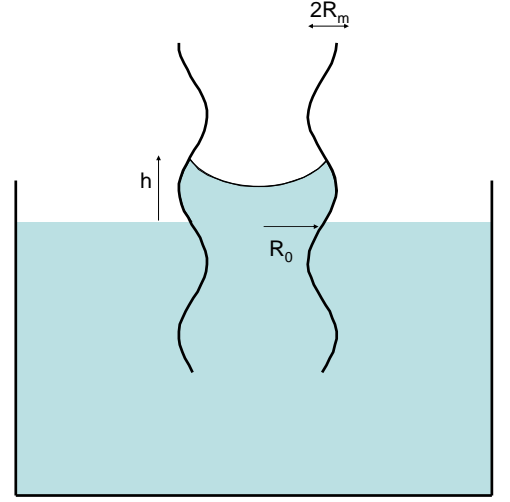


FIG. 4: Schematic illustration of a capillary with sinusoidal modulations of the radius.

where  $\bar{R}_m \equiv \kappa R_m$  and  $\mu = q/\kappa$ . It is clear from Fig. 2 (b) that there are multiple solutions, half of which are maxima and the other half minima.

For a system prepared in a given minimum, increasing  $\theta$  by the use of electrowetting decreases  $\cos \theta$ . Thus, the liquid location changes –  $h$  decrease. When the liquid height overlaps with a minimum of  $f(\bar{h})$ , further increase of  $\theta$  leads to a jump in the liquid height to the next “branch” of  $f(\bar{h})$ . In this way one “quantum” of liquid is depleted from the capillary; if  $\theta$  is decreased, at each step one liquid unit is sucked into the capillary. The unit volume can be estimated to be  $v \sim R_0^2/q$ ; for a capillary width of  $R_0 = 100 \mu\text{m}$  and wavenumber  $q = 10^3 \text{ m}^{-1}$ , we find  $v = 10 \text{ nL}$ , whereas reducing the sizes to  $R_0 = 10 \mu\text{m}$  and  $q = 10^4 \text{ m}^{-1}$  gives  $v = 10^{-2} \text{ nL}$ .

In summary, we have shown that the liquid height in capillaries with nonuniform cross-sections is a discontinuous function of the geometrical variables. This peculiar phase-transition is important for the understanding of liquids confined to small environments, as capillaries in practice rarely have uniform cross-sections. Indeed, since  $\alpha^*$  can be extremely small, if the surfaces of the capillary are super-hydrophobic, very small deviations of  $\alpha$  around  $\alpha = 0$  will yield discontinuous liquid heights. It may be beneficial to exploit the dependence of the water level on the contact angle (e.g.) in microfluidic applications where it is desired to accurately control small volumes of liquid. The setup of Fig. 1 could possibly be used as a “switch” to prevent or allow liquid flow or electrical current in the direction perpendicular to the plane of the paper, while the setup of Fig. 4 permits to “suck” known quantities of fluids.

In this paper we assumed ideal surfaces and thus have not dealt with rough surfaces and hysteresis effects [29]. It would also be interesting to consider a pressurized cap-

illary (micro-pipette), where the finite pressure difference between the capillary and the ambient atmosphere can bring about further surprises [30].

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